EXCESS HEAT DURING THE ELECTROLYSIS OF A LIGHT WATER SOLUTION OF K₂CO₃ WITH A NICKEL CATHODE

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Experimental results of differential heat loss calorimetry measurements during the electrolysis of light water solutions of K_2CO_3 and Na_2CO_3 with a nickel cathode are presented. A significant increase in temperature with every watt input, compared with the calibration experiment, is observed during the electrolysis of K_2CO_3. This effect is not observed when Na_2CO_3 is electrolyzed. No trivial explanation (in terms of chemical reactions, change in heat transfer properties, etc.) of this effect has been found so far. If the nontriviality of the observed overcoming of the energy breakeven barrier is further confirmed, this phenomenon may find application as an important new energy source.

INTRODUCTION

The studies in this paper follow the general lines of the work of Fleischmann and Pons,[1] although electrolysis of D₂O is usually considered when excess energy is claimed. Observation of excess energy production during the electrolysis of H₂O was first mentioned by Pons and later rejected.[1] Pons et al., however, explicitly state the possibility of obtaining excess energy during electrolysis of ordinary water (using nickel as a cathode, among other proposed metals) in Ref. 2. Unexplained excess heat in light water is also claimed in a paper by Bush et al.[3] Mills and Kneizys[4] claim to have obtained excess energy above the amount spent during the electrolysis of a K₂CO₃ ordinary water solution with a nickel cathode. The excess energy effect, according to these authors, is not observed when Na₂CO₃ is electrolyzed. Furthermore, unusual effects during the electrolysis of light water have also been reported by Matsumoto.[5]

This paper compares the heating coefficients for a nickel/platinum (Ni/Pt) circuit with those for a resistor heater in vacuum-jacketed dewar electrolytic cells containing K₂CO₃ or Na₂CO₃. Note that the excess energy effect from an electrochemical system containing K⁺ (Li⁺ is usually used in these studies) in D₂O is reported in Ref. 6.

EXPERIMENTAL DETAILS

The experiments were carried out by observing and comparing the temperature difference, $\Delta T_1 = T_{electrolysis\ only} - T_{blank}$ and $\Delta T_2 = T_{resistor\ heating\ only} - T_{blank}$ referred to unit input power, between two identical 200-ml silver-coated vacuum-jacketed dewars. A calorimeter dewar having the same configuration and containing the same amount of electrolyte, same type of electrodes (nickel cathode and platinum anode), resistor heater, and thermistor (thermometer) and stirred at the same speed was used as a blank; neither electrolysis nor heating by the resistor was carried out in this dewar. Experiments were also carried out by using as a blank a dewar used in a previous experiment and vice versa. This exchange was done to ensure that the effect was not due to any difference in the thermal properties of the two specific dewars used. Each dewar had a 3-cm opening, and a 2-cm-thick tapered rubber stopper was placed 1 cm into the dewar. The experimental apparatus for the differential calorimetry used in these studies is shown in Fig. 1. Unlike the studies in Ref. 4, the resistor and the electrolytic circuit were not run simultaneously in this study; the effects of heating by the resistor and by the electrolysis circuit were studied in separate runs.

As is usual in electrochemistry, measures were taken to avoid impurities in the system, especially organic substances. While it is unclear at this point what the relationship is, if any, between the contamination effect on the hydrogen overpotential and that on the eventual excess heat, one should recall the known problems with the reproducibility of the hydrogen overpotential, which can be overcome only by ensuring the lowest possible level of impurities. Certain procedures should be applied to reproduce the excess heat effect. For instance, before starting the experiment, mechanically scour the platinum anode with steel wool, soak overnight in concentrated HNO₃, and then rinse with distilled water. Remove the nickel cathode from its container with rubber gloves, and cut and bend it in such a way such that no organic substances are transferred to the nickel surface. Preferably, dip the nickel cathode into the working solution under an electrolysis current, and avoid leaving the nickel cathode in the working solution in the absence of an electrolysis current. Clean the electrolysis dewar, and free it of organic contaminants.

After assembling the experimental setup, the nickel cathode was subjected to anodizing by a constant electrolysis current of 0.083 A for 1 h. Then, the direction of the electrolysis

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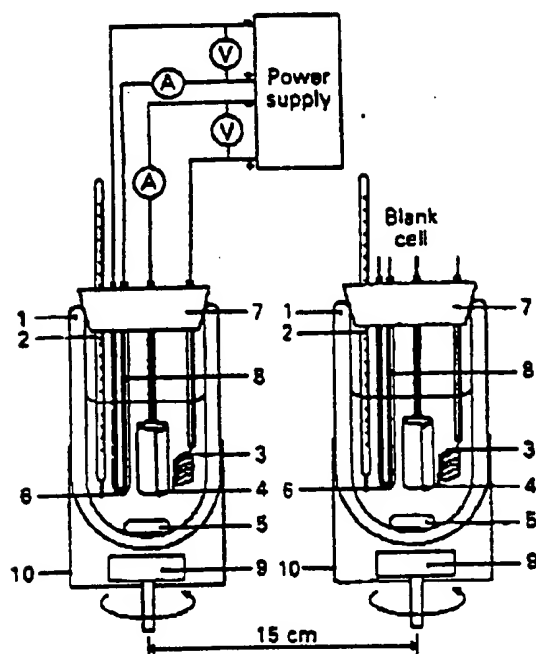Noninski   EXCESS HEAT WITH LIGHT WATER SOLUTION

Fig. 1. Experimental setup: (1) vacuum-jacketed dewar, (2) thermometer, (3) platinum anode, (4) nickel cathode, (5) magnetic stirring bar, (6) resistor heater, (7) rubber stopper, (8) Teflon tubing, (9) magnetic stirrer, and (10) aluminum cylinder.

current was reversed (platinum anode and nickel cathode), and the electrolysis was carried out for 14 to 16 h.

The electrolysis heating power was calculated as $P_{el} = (E_{el} - 1.48)I_{el}$, where E_{el} is the applied electrolysis voltage, I_{el} is the electrolysis current (the term "electrolysis power" is used here for convenience, denoting only the power contributing to the joule heating effect during the electrolysis), and 1.48 V is the isoenthalpic voltage, which at the temperatures studied practically coincides with the thermoneutral voltage. The resistor heater power was calculated as $P_h = I_R E_R$, where I_R denotes the resistor current and E_R denotes the resistor voltage.

The cathode was a 7.5-cm-long × 4-cm-wide × 0.0125-cm-thick nickel foil (Aldrich 99.9+ %) spiralled into a cylindrical form. The anode was a 0.1-cm-diam × 10-cm-long platinum wire (Johnson-Matthey). The spiral anode and the cylindrical cathode were parallel to each other. The leads were inserted into Teflon tubes to prevent any recombination of the evolving gases. The electrolyte solution in both dewars was 153 ml of 0.57 M K_2CO_3 or 0.57 M Na_2CO_3 in H_2O. The distilled water was from the common distiller of the Chemistry Department of Franklin and Marshall College. The power was delivered by a Zenith SP-2718 power supply (alternating current component <0.1%). The resistance heater was a 100-Ω, 1% precision, metal oxide resistor in a 2-mm-o.d. Teflon tube. The electrolyte solution in both dewars was stirred simultaneously (synchronized for the two dewars) by two identical spheroidal ellipse magnetic bars rotated by two magnetic stirrers at ~300 rpm. Electrolysis voltage and current were measured by two Keithley 169 multimeters, and the resistor voltage and current were measured by Extech 380198 and

Micronta 22-185 A multimeters with 0.01-V and 0.001-A accuracy, respectively. The use of vacuum-jacketed dewars, rather than air-jacketed dewars or simple flasks, made the measurements more sensitive (higher heating coefficient). In a vacuum-jacketed dewar unit, input power leads to a greater steady-state temperature, thus enabling differences in steady-state temperatures (for the same configuration) to be more pronounced. The temperatures in this study were monitored continuously using the capability of the standard calorimeters (Parr P-318) to record the temperature continuously (with 0.01°C accuracy) on their strip-chart recorder (Fisher Record-all Series 5000).

RESULTS AND DISCUSSION

The results of the study are shown in Figs. 2 through 5. Figure 4 is based on the data presented in Figs. 2 and 3. Figure 2 shows the absolute change in the measured temperatures of the dewars at different conditions, while Fig. 3 shows the input powers in each case. It can be seen from Fig. 3 that while the input power with the resistors working was constant as expected, the input electrolysis power was not, and there is a time lag between the application of power and the temperature response. We compensated for this by selecting appropriate power values when calculating the heating coefficients plotted in Fig. 4 (more precisely, the term "heating coefficient" refers only to the steady-state values of the quantities in Fig. 4; the last parts of the curves in Fig. 4 can be considered to represent steady state). The heating coefficients plotted in Fig. 4 were calculated using the average power plotted in Fig. 3. Note that other reasonable ways of referring the observed ΔT to the applied power are possible; however, even the most conservative approach gives the same qualitative effect as that seen in Fig. 4. Studies currently in progress, using a data acquisition system, show sustained steady-state production of excess heat for many days. Results from these studies are presented elsewhere.
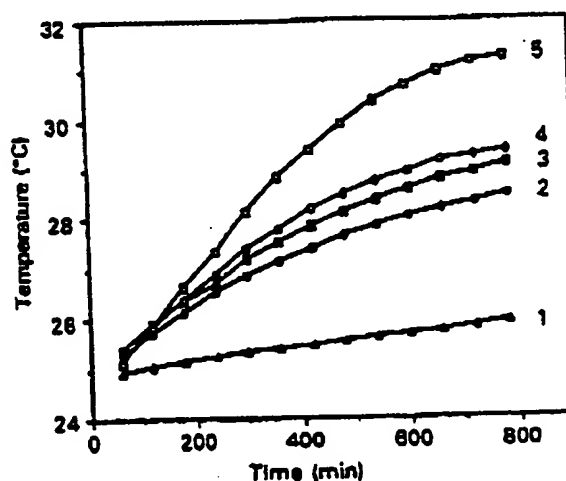

Fig. 2. Time history of temperatures: (1) blank cell (this curve is used as the blank for computing the heating coefficients of Fig. 4); (2) K_2CO_3 calibration cell (with only resistor heater working); (3) Na_2CO_3 calibration cell; (4) K_2CO_3 electrolysis cell (with only electrolysis working); and (5) Na_2CO_3 electrolysis cell.
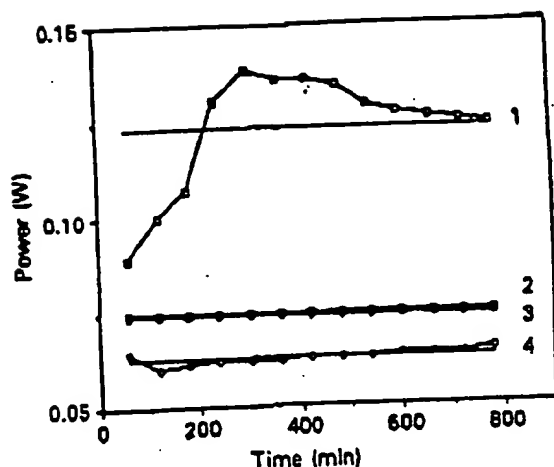
Fig. 3. Time history of the applied power: heating power with (1) electrolysis in the Na_2CO_3 cell, (2) the resistor in the Na_2CO_3 cell, (3) the resistor in the K_2CO_3 cell, and (4) electrolysis of the K_2CO_3 cell. The thermoneutral voltage is 1.48 V. For the calculations presented in this paper, mean values of the electrolysis powers in the Na_2CO_3 and K_2CO_3 cells are used, shown as solid lines in curves 1 and 4.
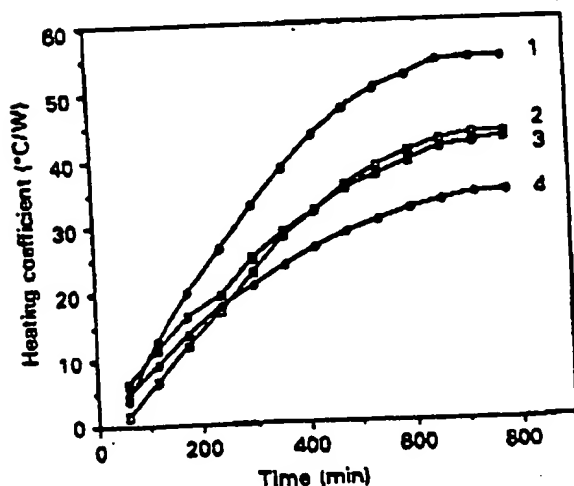

Fig. 4. Plot of the heating coefficients over time: (1) electrolysis at 0.083 A in K_2CO_3, (2) resistor working in Na_2CO_3, (3) electrolysis at 0.083 A in Na_2CO_3, and (4) resistor working in K_2CO_3.

The heating coefficient of the Na_2CO_3 cell is plotted in Fig. 4. The heating coefficient for the resistor heater only and that for the electrolysis circuit only are essentially identical. This is to be expected for a given dewar and a given electrolyte when steady state is reached: The ΔT corresponding to a unit heating power has a strictly defined value, determined by the properties of the materials through which heat is being lost. The properties of the cell are unaltered during operation. Specifically, the volume of electrolyte remains practically constant: ~0.2% of the solution volume is being electrolyzed during the 12-h operation of the Ni/Pt cell.

In contrast, the calorimeter containing K_2CO_3 showed very different behavior. The heating coefficient of the K_2CO_3 cell is plotted over time in Fig. 4. The heating coefficient-time curve of the working electrolysis cell is clearly above the curve of the dewar in which only a resistor is working. The value of the heating coefficient with the Ni/Pt circuit working is ~50°C/W, while the heating coefficient with only the resistor working is ~30°C/W. Therefore, the output power obtained through the Ni/Pt circuit is ~160% of the input power. The time-integrated power (i.e., energy) input into the system during the course of the experiment in Fig. 4 is ~4800 J compared with the output power of ~8000 J. Thus, Fig. 4 shows a significant difference in the thermal behavior of two identical systems that differ only in the positive ions of the salt.

A trivial explanation for this behavior of the K_2CO_3 cell is not straightforward. In fact, the electrolysis should be expected to lead to a decrease in the heating coefficients compared with those of the cells in which only the resistor is working ". . . consistent with additional heat losses caused by gas evolution . . . ,"[7] which is currently observed only in the Na_2CO_3 cell.

The erroneous attribution of the effect to temperature gradients was eliminated by testing for minute spatial variations of the temperature over time. Three thermistors were positioned ~2.5 cm apart at the bottom, middle, and upper part of the electrolyte. The results, shown in Fig. 5, clearly demonstrate that no difference is observed (within the limit of detection, 0.01°C).

Note that the electrolysis is always started with a newly manufactured cathode from the batch of 99.9%+ purity nickel. The use of new nickel excludes any possibility that the effect is due to the decomposition of species formed before the beginning of the electrolysis. The reaction of hydride formation is exothermic with a standard enthalpy of formation[8] of -8.79 ± 0.59 kJ·mol^{-1} H_2. However, if all of the hydrogen evolved during the run became hydride, an energy contribution would result that is more than one order of magnitude less than the excess heat that is observed according to Fig. 4. This can easily be calculated based on the amount of hydrogen evolved over ~12 to 14 h at a rate of 0.083 A. Although the overall amount of energy produced in the experiment is relatively low, it is clear that the observed effect is outside the error limit of the experiment, which is of the order of ± 1°C/W, calculated from the accuracies of the measured parameters at the respective ranges.

It is not known what trivial chemical reaction might be triggered by the applied electrolysis that would be capable of producing the observed amount of excess heat. Some exotic farfetched possibilities for explaining the difference in electrochemical behavior between K_2CO_3 and Na_2CO_3 can be postulated. One such example is the formation of formic acid, e.g., by the reaction $HCO_3^- + 2H_2O \rightarrow HCOOH + 3OH^-$, or methane if $KHCO_3$ is present in the electrolyte. However, even if such possibilities are invoked, it should not be forgotten that energy is also being spent for these electrochemical reactions, which will again result in an isoenthalpic (or thermoneutral) voltage. In most cases, the value of this thermoneutral voltage may exceed 1.48 V, which will cause cooling rather than heating of the solution. This is indicative of even higher excess energy values. A reaction that readily comes to mind is oxygen reduction. It is well known, however, that nickel is a poor catalyst of oxygen reduction, and the current density of this reaction is negligibly small compared with the current density applied here (~1 mA/cm²).
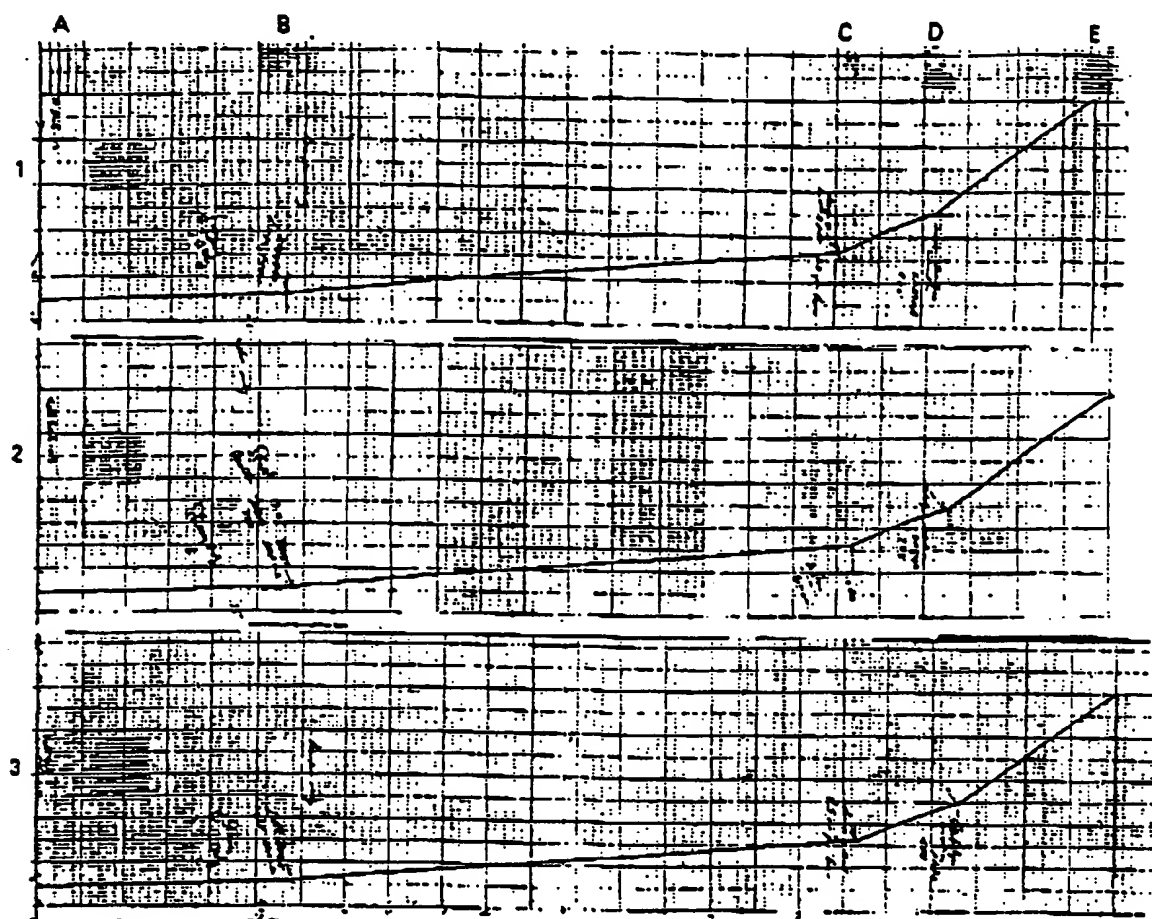
Fig. 5. Temperature changes at three points within the solution: (1) at the top, (2) in the middle, and (3) at the bottom. The setup used for this study is similar to that presented in Fig. 1, but in the working cell there are three thermistors instead of one. Section A-B: x axis scale = 30 division/h, y axis scale = 0.2°C/division, stirring only; section B-C: x axis scale = 30 division/h, y axis scale = 0.2°C/division, resistor only; section C-D: x axis scale = 5 division/h, y axis scale = 0.2°C/division, resistor only; and section D-E: x axis scale = 5 division/h, y axis scale = 0.2°C/division, electrolysis only.

These possibilities were rejected after study of the correspondence of the Faraday efficiency of the evolved H_2 and O_2 gases. This was done in a separate experiment by collecting the evolved gases and comparing the measured volume of the gases with the volume corresponding to the quantity of electricity that had passed through the cell over a given time. Note also that the absence of appreciable $H_2(D_2) + O_2$ recombination has been noted by a number of investigators, even in systems that contain metals (e.g., palladium) that are known to be good catalysts of that reaction (e.g., Refs. 9 through 14). Other preliminary studies (mass spectroscopy, pH measurements, titration) before and after the experiment showed no unexpected species or pH change. These studies should be continued further.

The problem of recombination is a crucial one in this study (note again that the excess heat here is calculated after subtracting 1.48 V), however, and it deserves special attention in any further experiments. On the other hand, as we have noted,[8] the problem of recombination (and the other connected calorimetric problems) preferably should not be solved by studying the effect in a closed cell with a recombiner. The recombiner adds new unknowns since the kinet-

ics of the recombination of H_2 and O_2 to H_2O should be well understood through studies such as those in Ref. 15. On the other hand, since the claimed excess energy itself is a newly found, unstudied phenomenon, no additional conditions should be imposed because their eventual effect on the reproducibility of the excess energy is unknown. For instance, it is not clear whether the ability of the recombiner to recombine not only the H_2 and O_2 evolving through electrolysis but also all other quantities of H_2 and O_2 existing in the gas and the liquid phase, thus creating concentration gradients, will be a hindering factor for the appearance of excess energy.

An explanation for the increase in the heating coefficient for a Ni/Pt circuit might be that an additional source of energy of unknown nature is acting from within that adds to the energy input to the cell from without. If this nontrivial possibility is confirmed, this effect will be of great importance as an alternative energy source. Further calorimetric sophistication is necessary to further confirm the reality of the observed effect and to obtain a quantitative assessment of its magnitude. For instance, to avoid errors of a subjective nature, a data acquisition and processing system is necessary. The measurements should be carried out at constant input

power and for longer periods of time so that curves like curve 1 of Fig. 2 reach a clear and sustained steady state. Maintaining a constant ambient temperature is also a requirement in these studies. Such studies are now in progress. To fully avoid concerns connected with the peculiarities of heat transfer during bubble evolution, it is necessary, together with heat loss calorimetry measurements (including Seebeck), that this effect be observed in an adiabatic-type calorimeter (bomb calorimeter) similar to the one used in Ref. 6. Note, however, that despite the opinions of some researchers, if careful studies are carried out, calorimetric techniques are not only capable but are the only ones that can decisively prove (or disprove) the reality of the effect in question. There is also no reason to expect that time spans of tens of hours will be insufficient to definitely rule out (or conclusively confirm) a trivial explanation of the observed effect if the studies are conducted carefully. It seems, however, that the reality of the effect can qualitatively be established with the described procedure. It seems also that the reported effect is reproducible and can easily be demonstrated.

It is the author's understanding that speculations (invoking reactions of nuclear or any other origin) as to why overcoming the energy breakeven barrier might come about should be carried out only after firmly establishing the reality of the claimed effect through experiments. This circumstance is not new for science. One may recall the experimental findings of Davison and Germer, Einstein, Wien, Compton, and others, which were unexplainable at the level of knowledge at their time. These experimental findings virtually caused the birth of 20th century physics, especially quantum mechanics. Even one of the most recent scientific discoveries— high-temperature superconductivity—whose reality is undeniable, still remains unexplained, which does not make this experimentally found effect less important.

Since the problem of the reality (nontriviality) of the excess energy reported here is of primary concern, we leave open the questions for the theoretical explanation of the phenomenon.

CONCLUSIONS

The experimental results presented here show that there is more evidence than usually considered for the eventual production of excess energy during the electrolysis of water. Therefore, further efforts seem to be justified for verifying the claim of Fleischmann and Pons for overcoming the energy breakeven barrier through electrolysis.

Contrary to the opinion expressed in Refs. 16 and 17, it does not seem plausible that light water should be used as a "control" when excess energy is being sought during the electrolysis of heavy water.

ACKNOWLEDGMENTS

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